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Practitioner's Docket No. 100325.0245PRO *PATENT*

Preliminary Classification
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Subclass:

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13441 U.S. PTO 60/538122 012004

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of: John Mak, Richard Nielsen, Thomas King Chow, Oliver Morgan, and Vincent Wai Wong

For: Methods and Configurations for Acid Gas Enrichment and Sulfur Recovery

Mail Stop Provisional Patent Application
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

COVER SHEET FOR FILING PROVISIONAL APPLICATION
(37 C.F.R. § 1.51(c)(1))

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 C.F.R. § 1.51(c)(1)(i). The following comprises the information required by 37 C.F.R. § 1.51(c)(1):

1. The following comprises the information required by 37 C.F.R.§ 1.51(c)(1):

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2. The names of the inventors are (37 C.F.R. § 1.51(c)(1)(ii)):

1. John Mak
2. Richard Nielsen
3. Thomas King Chow
4. Oliver Morgan
5. Vincent Wai Wong

3. The title of the invention is (37 C.F.R. § 1.51(c)(1)(iv)):

Methods and Configurations for Acid Gas Enrichment and Sulfur Recovery

4. The name, registration, customer and telephone numbers of the practitioner are (37 C.F.R. § 1.51(c)(1)(v)):

Name of practitioner: Martin Fessenmaier
Reg. No. 46697
Tel. 714-641-5100
Customer No. 34284

5. The docket number used to identify this application is (37 C.F.R. § 1.51(c)(1)(vi)):

Docket No. 100325.0245PRO

6. The correspondence address for this application is (37 C.F.R. § 1.51(c)(1)(vii)):

Rutan & Tucker, LLP
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USA

7. Statement as to whether invention was made by an agency of the U.S. Government or under contract with an agency of the U.S. Government. (37 C.F.R. § 1.51(c)(1)(viii)).

This invention was NOT made by an agency of the United States Government, or under contract with an agency of the United States Government.

8. Identification of documents accompanying this cover sheet:

A. Documents required by 37 C.F.R. § 1.51(c)(2)-(3):

Specification:	No. of pages	7
Drawings:	No. of sheets	3

9. Fee

The filing fee for this provisional application, as set in 37 C.F.R. § 1.16(k), is $160.00 for other than a small entity.

10. Fee payment

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METHODS AND CONFIGURATIONS FOR ACID GAS ENRICHMENT AND SULFUR RECOVERY

Field of The Invention

The field of the invention is gas processing and sulfur removal, especially as it relates to enrichment of an acid gas stream and tail gas treating from Claus plant.

Background of The Invention

There are numerous sources of natural or synthesis gas known in the art, and almost all of them contain H2S in various quantities that require at least partial desulfuration prior to further processing or release into the atmosphere. For example, natural gas, refinery gas, synthesis gas (*e.g.*, from gasification of residual oil or coke), or Fischer-Tropsch gas-to-liquids process (GTL) gases often contain H2S in significant amounts that would interfere with downstream processes. Furthermore, the sulfur content in the tail gas from the Claus reactors typically requires treatment before releasing the tail gas to the environment.

If H2S is present in large quantities, removal is commonly accomplished by absorption in an alkaline solvent, usually with an amine solvent. H2S is later regenerated or desorbed in a regenerator in a stripper operating at a lower pressure and elevated temperature. The acid gas from the regenerator is then typically processed in a Claus plant where the H2S is converted to elemental sulfur by sub-stoichiometric reaction with air or oxygen.

However, nearly all gas streams which contain H2S also contain significant quantity of CO2 and when such gases are simply scrubbed with an alkaline solution, CO2 is co-absorbed with the H2S. This is particularly problematic where the ratio of CO2 to H2S in the gas stream is relatively high, as complete removal of both gases will often produce an acid gas weak in H2S, which tends to cause various problems in the Claus plant. Among other things, the dilution effect of CO2 in such acid gases lowers the net heating value in the acid gas and also reduces the residence time in the Claus furnace, rendering sulfur conversion difficult. Moreover, such acid gases also contain significant quantities of contaminants (*e.g.*, benzene, toluene, xylene) that generally must be destroyed in the Claus furnace, which is necessary for protection of the Claus

reactor catalysts. Unfortunately, the CO_2 dilution effect in such acid gases tends to lower the furnace flame temperature, thereby making destruction of these contaminants difficult.

In extreme cases, where the H_2S content in the acid gas falls below 10%, a normal Claus reaction becomes impossible and additional processing steps must be employed to enhance the conversion process. Additionally, the dilution effect of CO_2 will increase the size of the Claus plant as the plant size is predominantly controlled by the total volumetric flow of acid gas.

Where the acid gas is unsuitable as feed to a Claus plant, preprocessing using a selective acid gas removal process is frequently necessary. In a typical preprocessing operation, two gas streams are produced via selective absorption of H_2S from the acid gas and subsequent stripping of the rich solvent. Thus, one gas stream predominantly comprises CO_2 that can be sent to a thermal oxidizer or incinerator for conversion of residual H_2S to SO_2, prior to being discharged to the atmosphere via a stack. The other gas stream is typically enriched in H_2S and is then processed in a simple Claus plant.

Generation of a sweet CO_2 stream can be particularly advantageous. Unlike the tail gas stream from a Claus plant, a sweet CO_2 stream is essentially free of nitrogen and can be further compressed and utilized for enhanced oil recovery, or as a diluent for controlling the flame temperature (NO_x control) in a gas turbine of an IGCC. Another advantage of selective gas treating is in the processing of Claus plant tail gas to meet environmental requirements. A typical Claus plant can recover about 95% of the sulfur contents in an acid gas stream. The residual sulfur content can later be removed and recovered in a tail gas unit, with the regenerated H_2S (via regeneration of the rich solvent) recycled back to Claus unit.

Known processes for selective H_2S removal from high CO_2 gases include the Stretford process, LOCAT and Sulferox unit. These processes employ complex catalyst-based chemistry to oxidize H_2S directly to sulfur. However, these units are often complex, difficult to operate, and are limited to relatively small capacity. Alternatively, various known amine based solvents capable of selectively removing H_2S can be used. For example, selective absorption processes can be based on blended tertiary amines (*e.g.*, those comprising diisopropanolamine (DIPA), formulated methyldiethanolamine (MDEA), and other amine-organic solvent blends). Such

solvents, particularly when combined with specially adapted absorber internal designs will minimize co-absorption of CO2 (typically, such processes can concentrate the H2S content by a factor of three to five fold). Other processes for selective H2S removal include the use of sterically hindered tertiary amino compounds described in U.S. Pat. Nos. 4,405,580.

In still further attempts to increase selectivity of absorption, special tray configurations can be employed to reduce the contact time with CO2 to achieve the required selectivity. For example, U.S. Pat. Nos. 4,278,621 and 4,297,329 and 4,678,648 describe special tray and packing designs in minimizing CO2 contact time. Unfortunately, the use of such processes and/or devices provide in most cases only marginal benefit for treating a diluted acid gas stream.

Alternatively, as described in U.S. Pat. Nos. 4,198,386 and 4,093,701, selectivity is achieved by varying gas flow-rates using a plurality of absorption columns, and splitting the absorber column into a number of absorption zones with controlled flow-rates of lean amine solvent. However, such systems typically require additional pipes and valves, and are often costly and complicated to operate. In yet further attempts to increase selectivity, H2S absorption may be enhanced via temperature control. Generally, a reduction in absorption temperature slows the CO2 absorption rate. However, the cost of operating a refrigeration unit render such an option often uneconomical.

Even where selective acid gas absorption is practiced with concurrent conversion of H2S to elemental sulfur in Claus plant, the residual sulfur content in Claus plant tail gases frequently poses additional problems. Among other things, the Claus plant tail gas often contains substantial quantities of H2S and therefore fails to qualify for emission standards that would allow such tail gas to be vented into the atmosphere. Numerous configurations are known in the art to reduce the sulfur content of such tail gas. However, most of such configurations are relatively complex and expensive to build and/or operate.

Therefore, and especially where a diluted acid gas feed is employed, currently known methods and configurations are often neither suitable nor economical. Thus, there is still a need to provide improved configurations and methods for selective acid gas enrichment.

Detailed Description

The inventors generally contemplate integrated configurations and methods of selective H2S absorption and sulfur recovery from various gases comprising H2S and CO2, and especially from gases in which H2S is diluted.

In one aspect, and with respect to selective H2S absorption, contemplated configurations employ an amine solvent (*e.g.*, methyldiethanolamine based solvent for preferential H2S absorption), and a dilute acid gas is first contacted with the lean solvent for selective removal of H2S, thereby producing (1) an overhead CO2 vapor with ppm level of H2S suitable for disposal in an incinerator, and (2) a H2S rich solvent that is processed in a regenerator. The regenerator produces a H2S enriched acid gas, a portion of which is contacted by a second amine contactor, producing an overhead CO2 vapor with ppm level of H2S suitable for disposal in an incinerator, and a H2S rich solvent that is recycled to the regenerator.

In an especially preferred aspect, the acid gas enrichment process is integrated with a Claus plant and a catalytic hydrogenation reactor, wherein the H2S enriched acid gas from the selective absorption process is sent to the integrated Claus unit. With respect to configurations and methods for selective H2S absorption from an acid gas comprising CO2, the same considerations as described in our copending U.S. provisional patent application with the title "Methods and Configurations for Acid Gas Enrichment" (filed on or about 01/20/2004 (John Mak et al.), and incorporated by reference herein) apply.

In particularly contemplated integrated configurations, the tail gas from the Claus plant is passed through a catalytic hydrogenation reactor and a quench column forming a tail gas containing a dilute concentration of H2S. The tail gas is treated in a third absorber, using lean solvent produced from the regenerator, producing an overhead CO2 vapor with ppm level H2S suitable for incinerator, and a H2S rich solvent that is recycled to the regenerator. Thus, it should be recognized that contemplated configurations lower the overall treating and sulfur recovery costs while minimizing emission problems. Based on various calculations, the inventors discovered that sulfur can be recovered up to 99.7% (and even higher) with significantly reduced capital and operating costs as compared to heretofore known configurations. Therefore, viewed

from another perspective, the inventors contemplate a two amine absorption stage enrichment process that enriches H2S in diluted acid gas to about 75%. It should be especially recognized that such process can be used with various solvents and associated equipment, including formulated MDEA (from Dow or INEOS) or from ExxonMobil's Flexsorb process.

Figure 1 shows an exemplary integrated configuration according to the inventive subject matter. The inventors discovered that combinations of an enrichment unit and a third absorber processing the tail gas from the Claus unit can effectively achieve a 99.7% or higher sulfur recovery with significantly reduced equipment.

Here, a two-stage Claus reactor system is used to process the enriched acid gas stream 18. It should be appreciated that a conventional sulfur plant without a tail gas treatment option would typically require four-stage Claus reactors and additional processing steps in order to achieve 99% sulfur recovery. In contrast, contemplated integrated tail gas absorption configurations significantly reduce overall cost when compared to conventional plants. The effluent gas from the Claus unit (stream 30), typically comprising trace quantities of sulfur oxides and unconverted H2S, is processed in a hydrogenation unit 71. The hydrogenated gas is quenched, cooled and the resultant gas is scrubbed in the tail gas scrubber 72, producing stream 31. The lean amine (stream 32), at a flow rate of about 300 GPM is supplied from the lean amine header to the absorber. The tail gas absorber overhead vapor stream 33 comprising trace levels of H2S can be routed to incinerator for disposal.

The rich amine stream 34 from the third absorber is pumped by amine pump 73 to about 50 psig forming stream 35 which is then combined with the rich amine 7 from the first absorber 51, forming stream 36. The combined stream is heated in the lean/rich exchanger and fed to the common regenerator.

Alternatively, **Figure 2** shows another exemplary integrated configuration with a Claus unit. In this configuration, the semi-loaded solvent 32 from the tail gas absorber 72 is re-used in the second absorber 22 and fed to the lower section of the second absorber. This economizes the solvent circulation and regeneration duties. With this arrangement, the incremental amount of solvent used in the tail absorber can be reduced, making the system integration more economical.

Figure 3 shows yet another exemplary integrated configuration with a Claus unit. This configuration is similar to Figure 4 with the exception that a portion of the semi-loaded solvent 7 from the first absorber 71 is re-used as stream 74. This semi-loaded solvent is cooled in a cooler 73 to about 100°F forming stream 75. This cold semi-loaded solvent is routed to the lower section of the second absorber 52. This configuration further reduces the solvent circulation and regeneration duties, making the integration energy efficient requiring the least solvent circulation.

Thus, it should be particularly appreciated that configurations according to the inventive subject matter will produce an acid gas enriched in H2S from a lean H2S stream, wherein the acid gas can be enriched from about 7% to about 75% H2S. Moreover, preferred configurations allow removal of hydrocarbons and BTEX components that is problematic with sulfur plant operation. Still further, it should be recognized that contemplated configurations will produce a CO2 stream with low H2S content suitable for disposal in incinerators. Alternatively, the CO2 stream may also be employed for enhanced oil recovery or as a diluent in a in gas turbine.

In present integrated Claus plant configurations, two otherwise necessary stages of Claus reactors can be eliminated, which substantially reduces overall plant cost. Still further, contemplated configurations solve the problems of low H2S content and lower heating content in the acid gas where the acid gas is diluted. Therefore, difficulties associated with fuel gas firing for the Claus reaction and BTEX destruction are eliminated. It should be further recognized that contemplated configurations and processes may advantageously be employed with various gas plants, sulfur plants, Gas-to-Liquid conversion plants, gasification plant, IGCCs, enhanced oil recovery plants, and various existing facilities that are retrofitted to meet more stringent emission requirements.

Thus, specific embodiments and applications of acid gas enrichment and sulfur recovery have been disclosed. It should be apparent, however, to those skilled in the art that many more modifications besides those already described are possible without departing from the inventive concepts herein. The inventive subject matter, therefore, is not to be restricted except in the spirit of the present disclosure. Moreover, in interpreting the specification, all terms should be interpreted in the broadest possible manner consistent with the context. In particular, the terms "comprises" and "comprising" should be interpreted as referring to elements, components, or steps in a

non-exclusive manner, indicating that the referenced elements, components, or steps may be present, or utilized, or combined with other elements, components, or steps that are not expressly referenced.

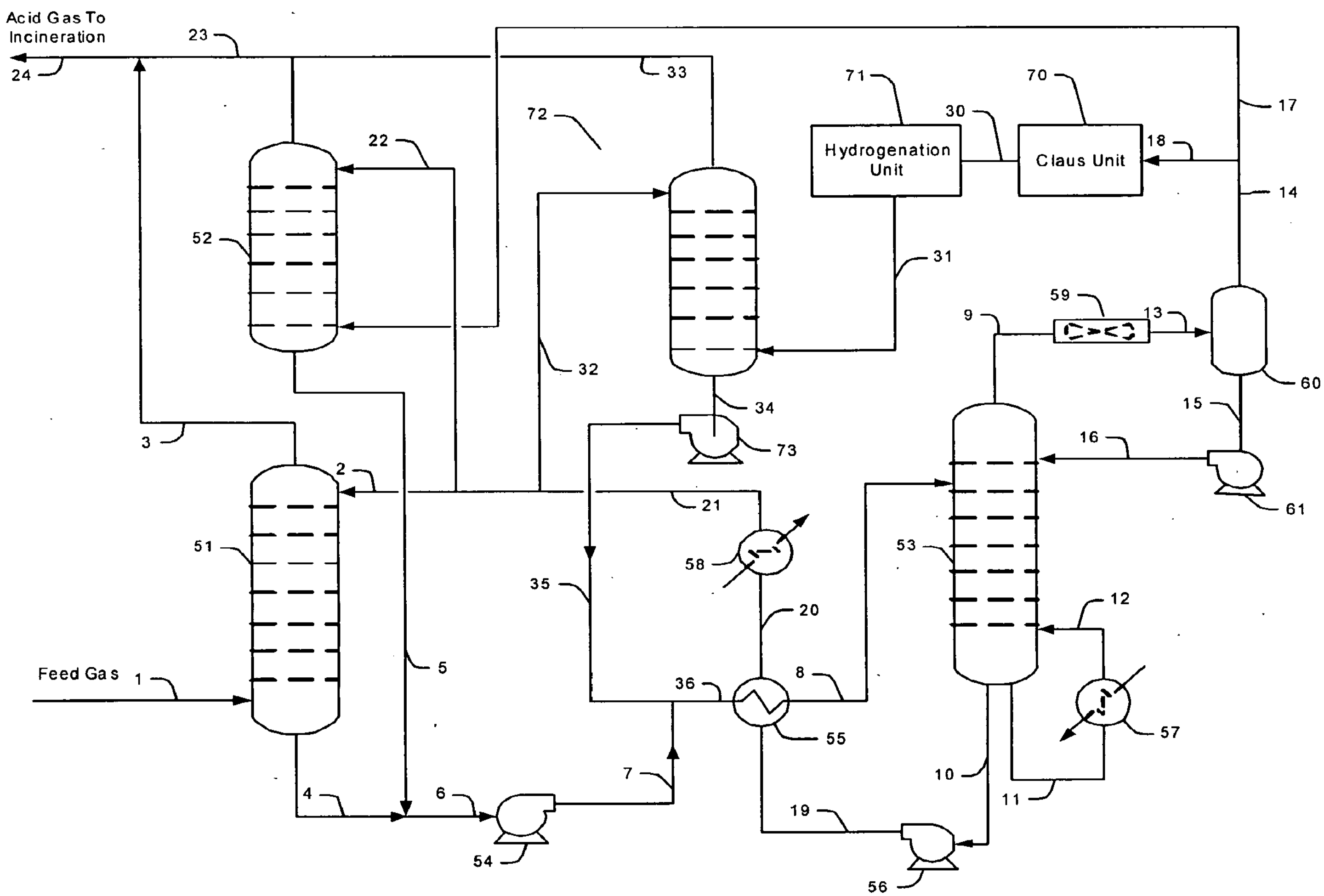

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Figure 1

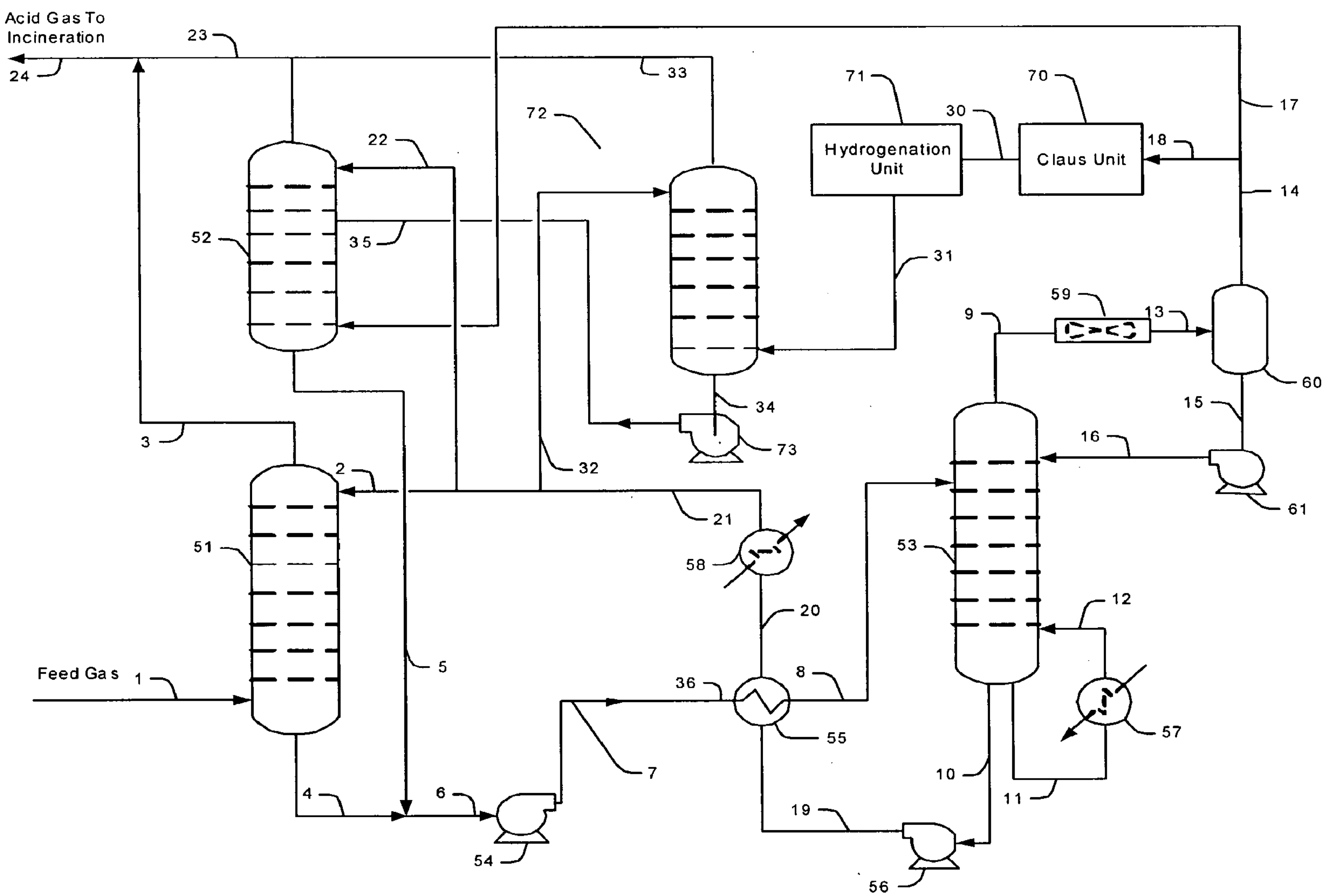
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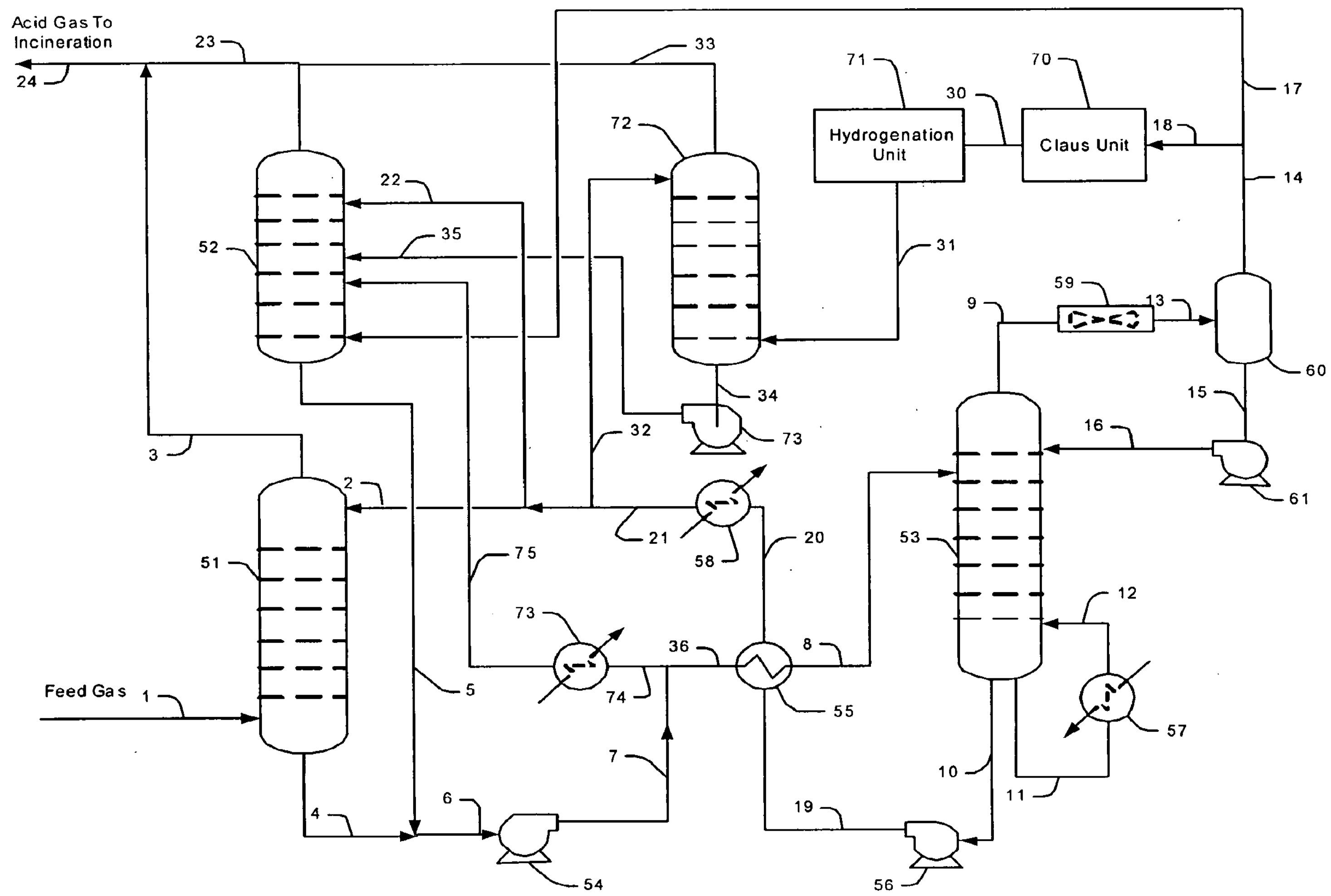
Figure 2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Feed Gas
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Figure 3